Senior Thesis

Oxidation of Magnetite in Wisconsinan Till, Union County, Ohio

by
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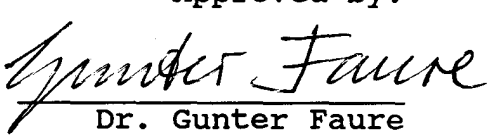

Dr. Gunter Faure

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Abstract

The concentration of magnetite of Late Wisconsin till samples, taken from a one-meter pit in Dover Township, Union County, vary irregularly from 3.5 to 6.9 percent of the heavy mineral fractions. However, the abundance of magnetite in the 63 to 250 μ m fractions of till increases systematically with depth from 44 percent of the magnetite in near-surface till to 68 percent at a depth of one meter. The abundance of magnetite of the 250 to 1000 μm fractions decreases in a complementary fashion from 56 percent at the surface to 32 percent at the bottom of the pit. The shift in grain-size distribution of magnetite grains correlates with leaching of calcite whose concentrations increase from zero at the surface to 30 percent at a depth of one meter. Therefore, I attribute the change with depth of the magnetite grain-size distribution to preferential oxidation of small grains to hematite as a consequence of chemical weathering since deposition of the till about 14,000 years B.P.(Goldthwait, et.al., 1965). The preferential destruction of small magnetite grains (68-250 μm) compared to larger ones (250-1000 μm) is promoted by the larger surface to volume ratio of the small grains and by the fact that small grains are consumed sooner than large grains at a constant rate of oxidation.

Introduction

Magnetite and calcite are common minerals in the tills of Ohio. The magnetite grains originate from the Precambrian igneous and metamorphic rocks of the Canadian Precambrian shield and were transported to Ohio by the Laurentide ice sheet during the Pleistocene glaciations. Calcite grains originated from marine limestone deposits of Devonian, Silurian, and Ordovician ages in Ohio and southwestern Ontario. The presence of limestone ($CaCO_3$) clasts in a till can easily be detected by the characteristic effervescence in the presence of an acid. Calcite has a solubility of approximately 18.5 μg/ml in water at the surface of the earth, so it can be used to determine the depth of leaching that has taken place in a till. The dissolution process of calcite can be expressed by the equation:

$$CaCO_3\ (s) + H_2O + CO_2\ (g) = Ca^{2+}\ (aq) + 2HCO_3^{2-}\ (aq) \quad (1)$$

The amount of calcite that is dissolved is controlled by the partial pressure of CO_2 in the environment where calcite is being put into solution. In soils, the partial pressure of CO_2 is elevated from the decay of organic matter, and therefore drives equation (1) to the right, gradually consuming $CaCO_3$ and CO_2 while calcium and bicarbonate ions are produced in the process. The gradual consumption of available CO_2 provides a reason for the gradual increase in the carbonate concentration with depth.

Magnetite is also removed from the till by a chemical process, although magnetite is less susceptible to chemical alteration than calcite. Magnetite is transformed to form hematite by the oxidation of iron. This process is represented by the equation:

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \quad (2)$$

In this reaction, the divalent iron in magnetite is oxidized by molecular oxygen (O_2) to form trivalent iron in hematite. Assuming that there is enough oxygen to drive the equation to the right, oxygen is gradually consumed while hematite is produced. The standard Gibbs free energy change for this reaction is calculated from the standard free energies of formation of each of the reactants and products and can be used to determine the equilibrium constant for the reaction.

$$\Delta G_R = \{6(-177.6)\} - \{4(-242.69)\}$$

$$\Delta G_R = -94.84 \text{ kcal}$$

$$K = 10^{-(-94.84/1.364)}$$

$$K = 10^{69.53}$$

$$[O_2] = 10^{-69.53} \text{ atm.}$$

The Law of Mass Action shows that magnetite is unstable when the partial pressure of oxygen becomes greater than $10^{-69.53}$ atmospheres. At the surface of the earth the partial pressure of oxygen is approximately 0.2 atm, which is far above the concentration necessary to make magnetite unstable.

Therefore, the purpose of this study is to examine the effects of weathering on the grain size distribution of magnetite as it alters to hematite in glacial tills. In addition, the calcite concentration is combined with the pattern of the magnetite concentration to display the correlation between the magnetite concentration and the effect of leaching of calcite.

Methods

Samples of till were taken along Myers Rd. in Dover Township of Union County east of Mill Creek on the Paradox Ranch in the ground moraine between the Powell-Union City and Broadway moraines. The general location of this site is shown in Figure 1. This ground moraine was deposited during the Wisconsinan stage of Pleistocene age about 14,000 years before present. The samples were taken from depths of 10.2 cm, 38.1 cm, 58.4 cm, 76.2 cm, and 96.5 cm, and were numbered from 1 through 5 with increasing depth. Each sample represents about 3 cm of stratigraphic thickness and the total amount of till recovered was about 10 kg per sample.

The concentration of calcite was determined by leaching a known weight of dried till with 0.5 N HCl. The samples were stirred each day until effervescence stopped. The sediment was then thoroughly washed by adding tap water, followed by stirring the sediment, letting it settle, and siphoning off the supernatant solution. This process was repeated three times for each sample to insure that all of the HCl and $CaCl_2$ had been removed from the sediment. After washing, the samples were dried on a hot plate for twenty-four hours. The leached and dried samples were weighed on a triple beam balance to within .05 g in order to determine the weight loss, which was assumed to be equal to the amount af calcite that had been dissolved. The concentration of calcite in the till was expressed as the weight percent of the till before leaching.

The grain-size distribution was determined by wet sieving. Prior to sieving, the samples were soaked in water to dissagregate them. The resulting slurry was passed through 1000 μm, 500 μm, 250 μm, 125 μm,

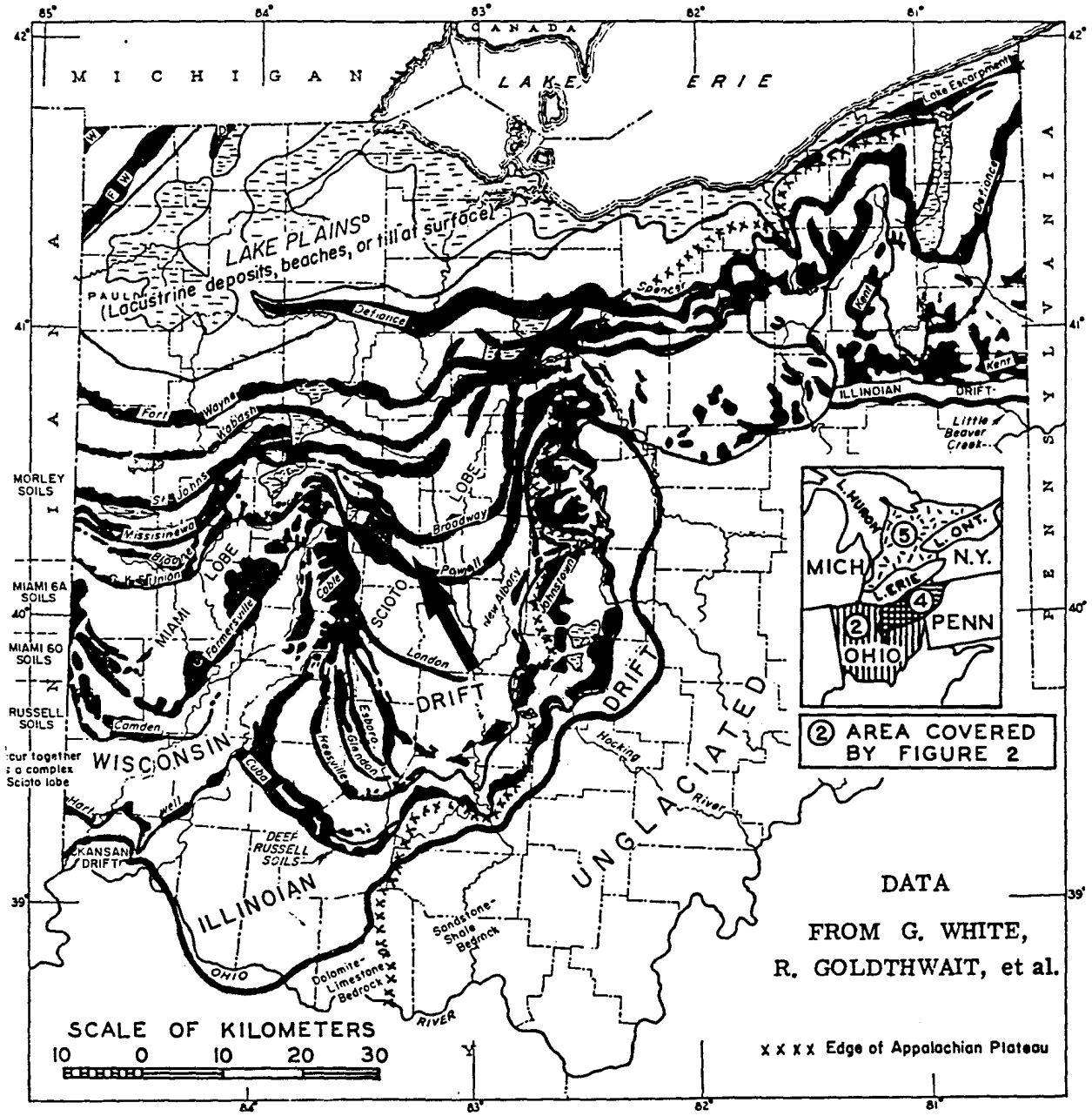

Fig. 1 Glacial map of Ohio shows the general location of the study in relation to Wisconsin moraines (from Goldthwait and others, 1965)

63 μm micrometer sieves. Each size fraction was dried for twenty-four hours, weighed, and the abundance of the size fractions in a given sample was expressed as the percent by weight of the total sample.

The heavy minerals were extracted from the 1000 μm to 500 μm, 500 μm to 250 μm, 250 μm to 125 μm, 125 μm to 63 μm micrometer size fractions by suspending them in full-strength bromoform (sp. gr. 2.83 g/cm^3) in a separatory funnel placed in a fume hood. The heavy minerals that sank to the bottom of the funnel were collected on filter paper and were washed repeatedly with reagent grade acetone in order to remove the bromoform. The acetone was then evaporated on a hot plate in a fume hood. The heavy mineral fractions were weighed, and their abundances were expressed in terms of weight percent of the total weight of all of the heavy mineral fractions of each sample.

Magnetite grains were separated from the heavy mineral fractions by a hand-held magnet with a plastic cover which was passed over the sample spread out on a sheet of paper. After the entire area of the sample had been scanned, the magnetite was recovered by removing the magnet from the cover. This procedure was repeated five times for each sample. The magnetic fractions of the heavy minerals were ground manually in an agate mortar to liberate any non-magnetite minerals that may have been associated with the magnetite grains. The magnetic fractions were extracted a second time from the resulting powders and were then weighed to within 0.00005 g, using an analytical balance. The concentrations of magnetite were expressed as weight percents of the total weights of magnetite in each sample. The data are compiled in the Appendix.

Presentation of the Results

Calcite Concentration

The calcite concentrations of the samples are displayed in Figure 2 as a function of depth below the surface. The diagram shows that the content increases from 4 percent at a depth of 10.2 cm to 30 percent at 91 cm below the surface. When the samples were taken, I observed that the till was homogenous and showed no signs of stratigraphic layering. Assuming that the till was homogenous with respect to its calcite concentration at the time of deposition, the data in Figure 2 imply that the calcite near the surface was lost by leaching of the till to a maximum depth of about 91 cm. Below this depth the till has maintained its original calcite concentration, whereas above this level the calcite has been dissolved by meteoric water moving through the till. Therefore, the depth of leaching is a function of time assuming that all other variables remain constant.

The abundance of clasts greater than 4mm in diameter show a pattern similar to the calcite concentration with depth. I classified all clasts larger than 4mm for each sample into sandstone, limestone, shale, and igneous/metamorphic varieties. The resulting distribution of lithologies with depth is shown in Figure 3. The dominance of carbonate clasts in unweathered till collected at the greatest depth may indicate that the bedrock along the flowline of the ice nearest the site of deposition is limestone. In the near surface till, sandstone is

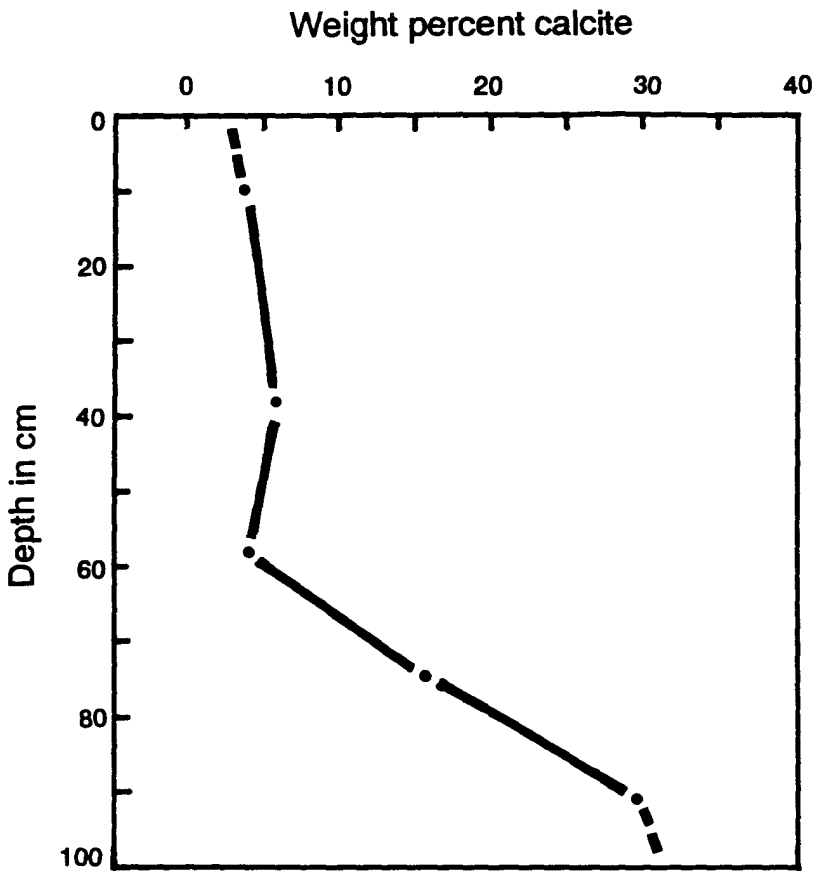

Fig. 2 Presentation of the weight percent of calcite for each sample of bulk till with depth. Dissolution of calcite results in lower concentrations of calcite in the samples near the surface.

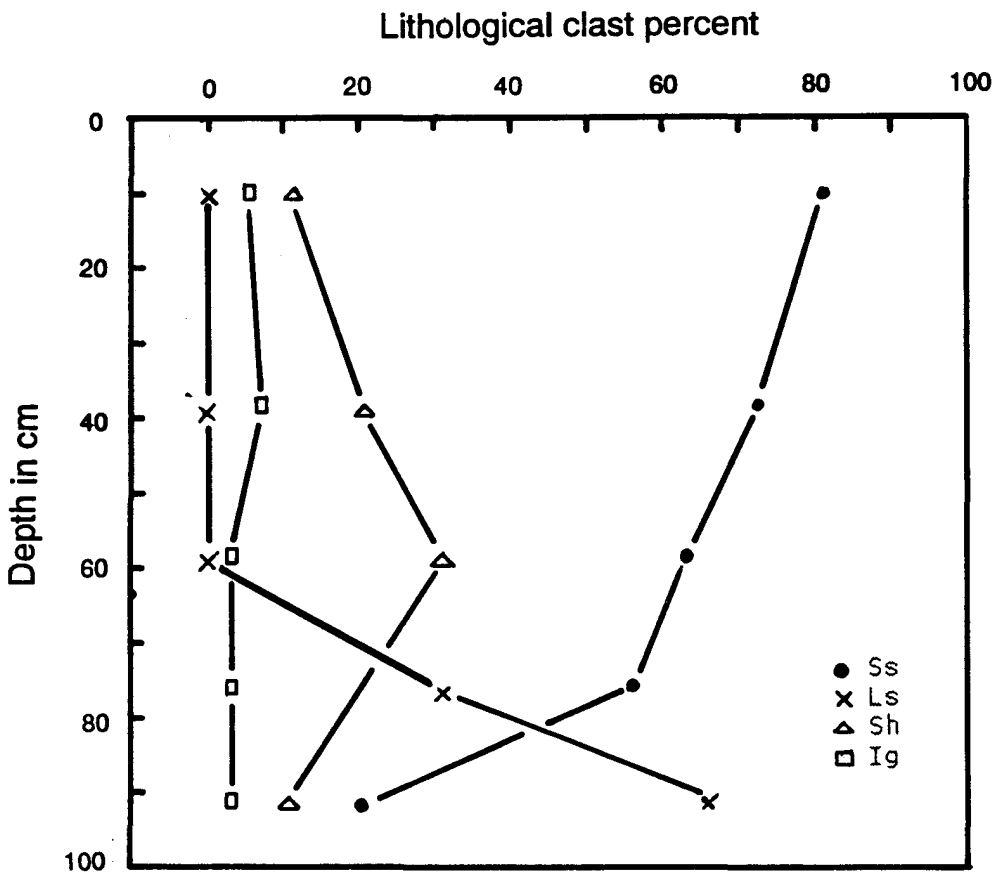

Fig. 3 Presentation of the distribution of clasts greater than 4mm in diameter with depth. The decrease in limestone clasts in near-surface samples is the result of leaching.

the dominant lithology of the clasts because the limestone clasts have dissolved. With increasing depth, the concentration of limestone clasts increases much like the concentration of calcite grains in the matrix of the till. Therefore, the abundance of the calcite clasts larger than 4 mm varies in the same way as the total calcite concentration of the till matrix.

Grain-Size Distribution

The grain-size distribution of the till is also affected by weathering as shown in Figure 4. The weight percent of the coarsest (500 μm to 1000 μm) fractions increase with depth. At the same time, there is complementary trend for the concentrations of grains in the smaller size fractions to decrease with depth. These changes are also indicators of the amount of leaching that has taken place since the time of deposition of the till. Since there is no evidence of stratification or sorting, I assume that the till originally contained a homogenous distribution of grain sizes that have been preserved in the least-weathered sample taken at a depth of 91 centimeters. Leaching begins at the surface of the deposit and moves deeper into the deposit with increasing time. Therefore, it is reasonable to think that the increase in the abundance of >1000 μm size fraction with depth is caused by the loss of limestone grains by weathering at the surface as indicated in Figure 3.

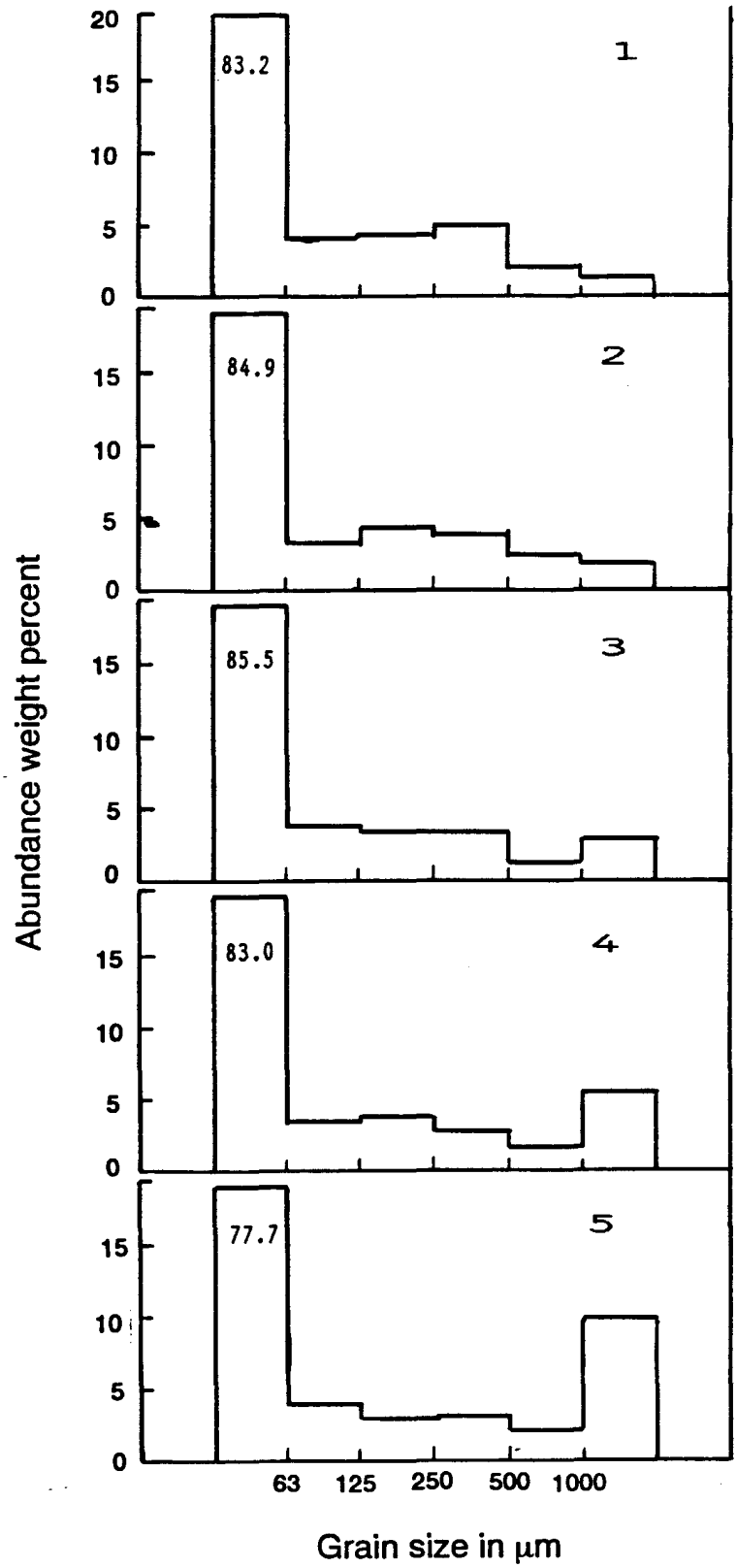

Fig. 4 Presentation of the grain size distribution of the bulk till for each of the samples. A decrease in the >1000μ size fraction results from the a loss of calcite clasts near the surface due to leaching.

Heavy Minerals

The heavy mineral fraction is composed of minerals with a specific gravity greater than 2.83 g/cm^3. A visual examination of this fraction shows that the major constituents are biotite, pyroxenes, hematite, and magnetite. There is no apparent variation in the concentrations of any of these minerals with sample depth, indicating the mineralogical homogeneity of the heavy mineral fractions. Figure 5 shows the size distribution of the heavy minerals for each sample. There is no evidence of any systematic variation in the grain-size distribution of the heavy minerals with depth. The absence of variation in grain-size distribution may be caused by the resistance of these minerals to glacial communition, chemical weathering, oxidation, or dissolution.

Magnetite Concentration

The concentration of magnetite grains in the heavy mineral fractions of the till samples varies irregularly with depth below the surface as shown in Table 1. Figure 6 displays the weight percent concentration of magnetite for each grain size fraction. However, after dividing the grains into a fine size fraction (63 μm to 250 μm), and a coarse size fraction (250 μm to 1000 μm), a pattern develops between them. Figure 7 shows that there is a complementary relationship between the concentration of magnetite in the coarse and fine size fractions so that they add up to 100 percent. In this method of presentation the concentration of magnetite in the coarse size fractions decreases with depth, whereas the concentrations of magnetite grains in the fine size fractions increase with depth. The intersection of these two lines form a point where the concentrations of magnetite in the coarse size

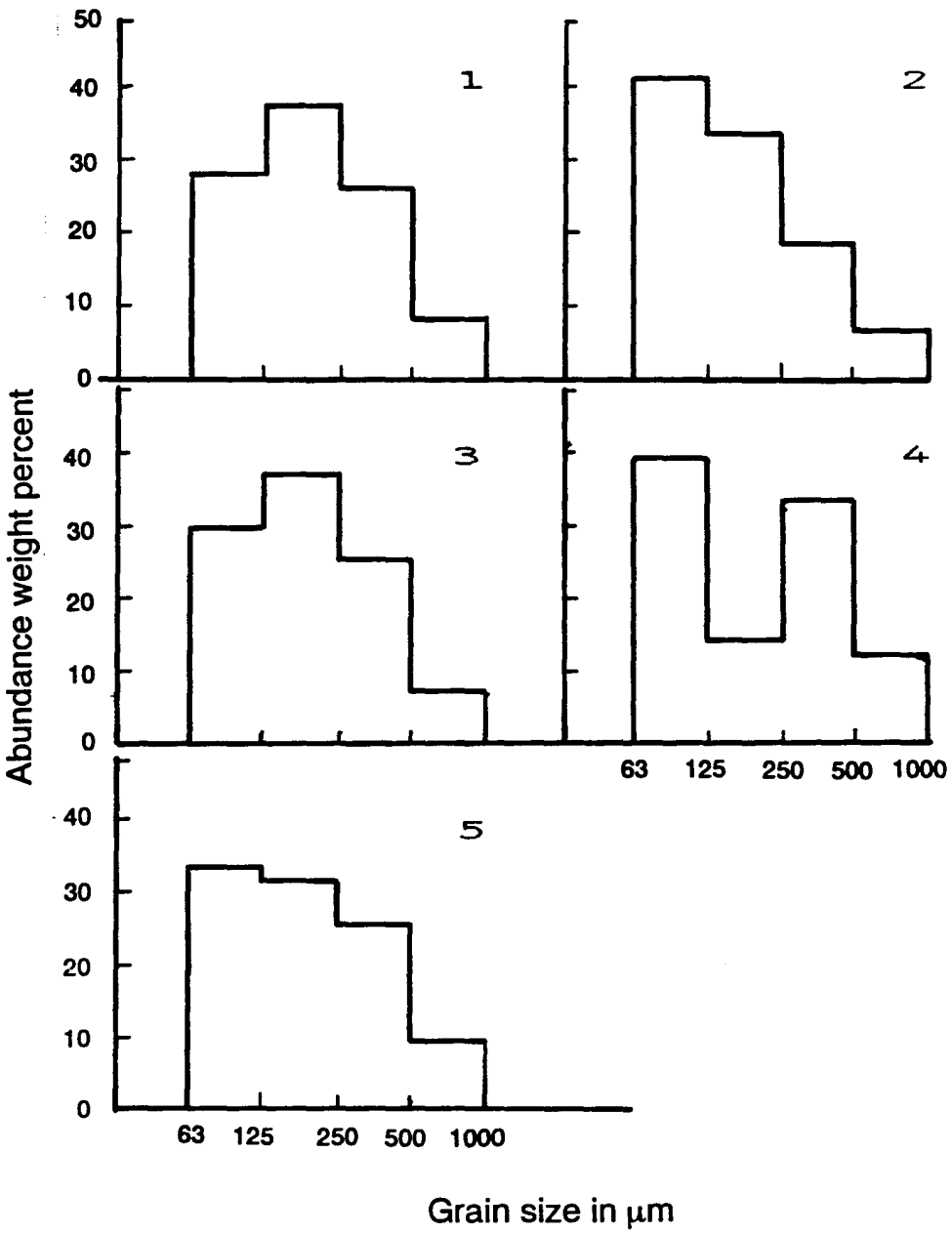

Fig. 5 Presentation of the weight percent of the heavy minerals in relation to grain size.

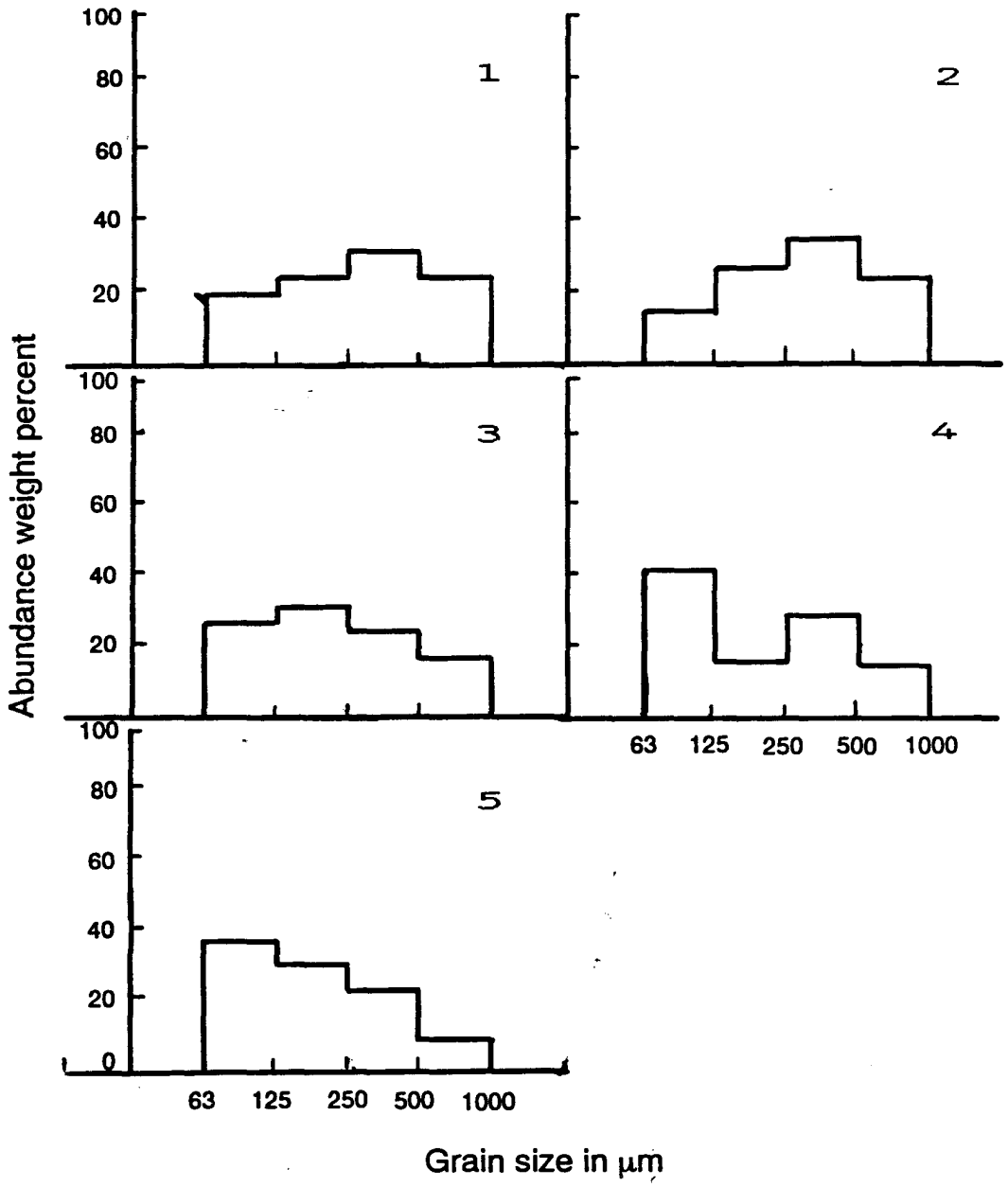

Fig. 6 Presentation of the grain size distribution of the magnetic fraction with a decrease in the concentration of grains in the fine size fractions and consequential increase in the concentrations of magnetite in the coarse fractions from preferential oxidation.

Table 1
Magnetite concentration

sample number	Percent of heavy minerals	Percent in coarse fraction	Percent in fine fraction
1	6.9	55.9	44.1
2	4.4	58.4	41.6
3	3.5	41.7	58.3
4	3.5	43.2	56.9
5	5.2	32.3	67.7

Table 1 Displays the magnetite concentration in the heavy mineral fraction and compares them to the concentration in the magnetic fraction after each sample has been divided into a coarse and fine size fraction.

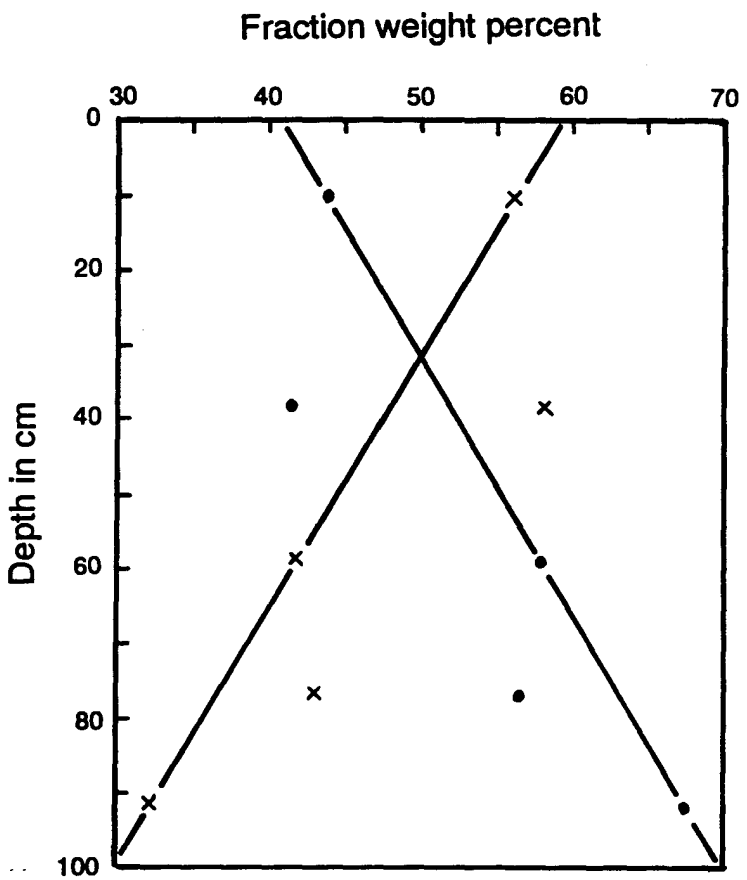

Fig. 7 Displays the change in the concentration of magnetite after dividing the samples into a fine size fraction and a coarse size fraction. The fine size fraction is represented by points and the coarse size fraction is represented by crosses.

fraction and fine size fraction are equal. At greatest depth the relationship between the coarse and fine size fractions most likely represents the distribution of both size fractions in the till at the time of deposition. These lines fit to the data of samples 1, 3 and 5 very well, but samples 2 and 4 give anomalous results. In both samples there is either too much magnetite in the coarse size fraction or not enough magnetite in the fine size fraction. A point with too little magnetite may indicate that additional weathering has taken place at this depth compared to the rest of the till. Additional weathering may be a result of a fracture in the till where meteoric water could be transported through the till readily. However, if this were the case, a decrease in the calcite concentrations of these anomalous samples would be expected. Sample 3 is in the zone of maximum leaching where all the calcite has been removed from the till, so it is impossible to determine whether additional leaching has taken place. Sample 4 does not show additional leaching of the calcite, so this anomalous point in the magnetite concentration is probably not a result of increased oxidation of magnetite grains. Even though there is no apparent stratification, random distribution may have resulted in the addition of magnetite in the coarse size fraction or the depletion in the fine size fraction, but there is no evidence to insure that this is the case. Figure 8 shows an alternative form of displaying the variation in magnetite grain with depth. By dividing the fine size fraction by the coarse size for each sample, the exponential decrease of this fraction with decreasing depth becomes apparent. At the maximum sampling depth (91.4 cm) the ratio of the magnetite concentration in the fine and coarse size fraction most likely represents their concentrations at the time of deposition and

should be constant for the remaining thickness of the till. Both of the diagrams also show the depth at which the concentration of magnetite in the fine fraction equals the coarse fraction. In Figures 8 a,b and Figure 7, this depth is 31 cm from the surface. The relationship between both size fractions near the surface is the result of the alteration of magnetite to hematite. The reaction takes place due to a change in the oxidation state of iron, when magnetite is exposed to O_2 at surface of the earth. This reaction is dependent on the surface area of the grain being oxidized. This means that grains with the greatest surface area are more susceptible to alteration. Therefore, the smallest magnetite grains,which have the greatest surface to volume ratio, are more susceptible to alteration than coarse grains. The alteration removes a layer of a certain thickness from each magnetite grain in the till in unit time. Therefore, large grains take longer to be destroyed during a given period of time. Consequently, weathered till is depleted in small magnetite grains. Since the extent of weathering decreases with depth, the abundance of small magnetite grains increases whereas the abundance of coarse grains decreases proportionately.

Whiting and Faure (1990) concluded that the abrasion of magnetite during transport by the ice sheet resulted in an increase in the concentration of magnetite in the fine fraction and a corresponding decrease in the magnetite concentration of the coarse size fraction with increasing transportation distance. In the present study the effects of grinding on grain size distribution was eliminated by taking all of the samples from a single location, so that the decrease of small magnetite grains can be attributed entirely to weathering since deposition.

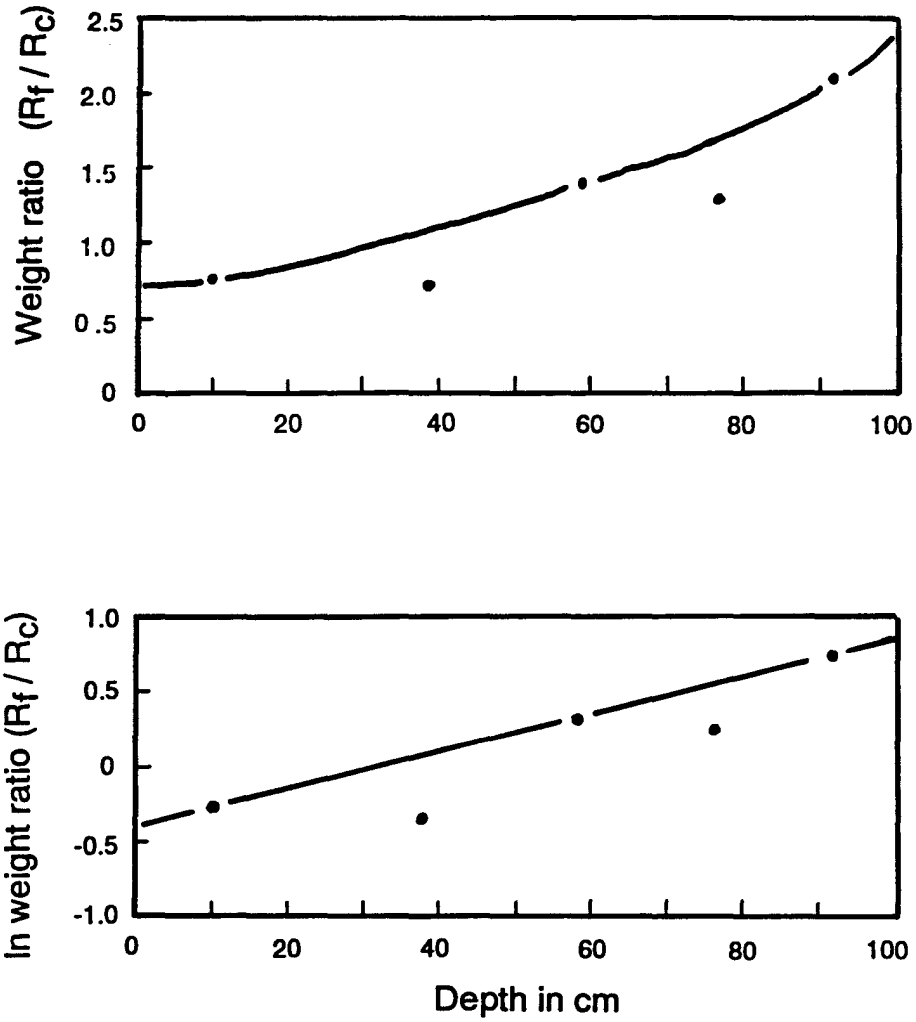

Fig. 8 a,b Presents an alternative form of the change in the concentration of magnetite in the coarse and fine size fractions with depth by dividing the fine size fraction by the coarse size fraction.

Other parameters which must be constrained are the time since the deposition of the till and its permeability. The longer a till is exposed to weathering, the greater the effects will become. By taking samples at a single location from a homogenous till that contained only one soil horizon, only one episode of weathering is present and variations in permeability are minimized that may occur between separate till deposits. The rate at which oxygenated and carbonated water moves through a till depends on the permeability of that till, and therefore affects the depth of leaching. If permeability is taken as a function of the concentration of clay-size particles, then the samples used in this study, with the concentration of clay-size particles ranging from 77.73 percent to 85.48 percent, do have the desired uniform constant permeability.

Another form this type of a study can take is to hold the amount of leaching constant while letting the age of the till vary. Similar relationships would develop between the coarse and fine size fractions, although they would be dependent on time rather than depth. These relationships form a type of a geochronometer calibrated by the amount of magnetite alteration that has taken place in tills of known ages.

Summary of Conclusions

I have shown that the maximum depth of leaching in the till of this study is approximately 91.4 cm based on the variation in the concentration of calcite with depth. This variation in the calcite concentration is dependent on the amount of carbonated ground water that percolates through the till. The change in grain size with depth can be attributed to the solubility of calcite and consequential loss of the

limestone clasts in the largest grain-size fraction. The closed table effect mandates that the smaller grain size fractions should increase in weight percent if the largest grain-size fraction decreases in weight percent in order that their sum remain 100 percent. The magnetite concentration varies randomly as the weight percent of the heavy minerals for each sample. However a pattern, dependent on the grain size, develops in the magnetite concentrations due to exposure of the magnetite to oxygenated meteoric waters. The small grains, which have a greater surface area to radius ratio than the large grains. In addition, the fact that smaller grains have less volume to be altered than the large grains results in the preferential loss of small magnetite grains near the surface of the till.

Acknowledgements

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Sample Number	Depth	$CaCO_3$ bulk wt. %	Grain Size Distribution, weight percent (in micrometers) <63	63-125	125-250	250-500	500-1000	>1000
1	10.2	4.0	83.2	4.1	4.4	4.9	2.0	1.4
2	38.1	6.0	84.9	3.3	4.1	3.8	2.3	1.7
3	58.4	4.3	85.5	3.7	3.4	3.4	1.3	2.8
4	76.2	15.9	83.0	3.5	3.7	2.7	1.6	5.5
5	91.4	29.9	77.7	3.9	3.1	3.2	2.1	10.0

	Concentration of Clasts Lithologies, Number percent of the total clasts sandstone	limestone	shale	igneous/meta
1	81.1	0.0	13.2	5.7
2	72.1	0.0	20.1	7.0
3	64.4	0.0	32.7	3.0
4	55.7	31.4	9.3	3.6
5	30.5	66.0	10.6	2.8

	Heavy Mineral Distribution, weight percent of total heavy minerals (in micrometers) <63	63-125	125-250	250-500	500-1000	>1000
1	n.d.	28.1	37.3	26.3	3.3	n.d.
2	n.d.	41.3	33.3	18.7	6.7	n.d.
3	n.d.	29.8	37.0	25.3	7.8	n.d.
4	n.d.	39.3	14.8	33.6	12.3	n.d.
5	n.d.	33.6	31.6	25.4	9.4	n.d.

	Magnetite, Weight Percent of Heavy Mineral Fraction	Magnetite Distribution, Weight Percent of Total Magnetite <63	63-125	125-250	250-500	500-1000	>1000
1	6.9	n.d.	27.7	31.23	24.4	14.6	n.d.
2	4.4	n.d.	24.0	34.4	26.9	14.7	n.d.
3	3.5	n.d.	16.6	25.0	31.7	26.6	n.d.
4	3.5	n.d.	14.3	28.9	15.3	41.5	n.d.
5	5.2	n.d.	8.7	23.6	30.7	37.0	n.d.

	Magnetite weight ratio (R_f/R_c)	
	(R_f/R_c)	$\ln(R_f/R_c)$
1	1.27	.24
2	1.40	.34
3	.71	-.34
4	.76	-.28
5	.48	-.74